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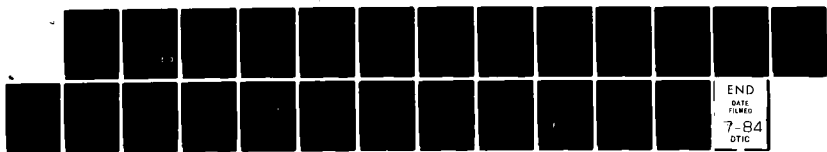
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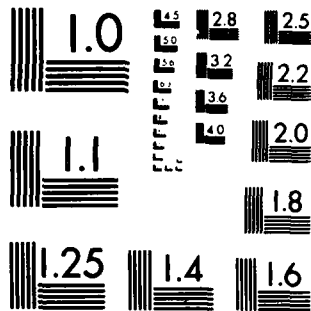
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THE ROLE OF BOUNDARY LAYER CAPACITANCE AT BLOCKING ELECTRODES IN THE
INTERPRETATION OF DIELECTRIC CURE DATA IN ADHESIVES

by

D. R. Day, T. J. Lewis, H. L. Lee, and S. D. Senturia

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Cambridge MA 02139

May 31, 1984

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evaluation of the effects of blocking layers on the interpretation of such dielectric data. The approach follows that used for dilute electrolytes, which is a reasonable model for the liquid resins, in which ion conduction will always be present to some degree. It is shown, first, that blocking layers can be modeled as capacitances in series with the bulk adhesive; second, that when the dielectric loss factor of the material is high (which is typically true early in cure), the apparent dielectric response is dominated by the charging and discharging of boundary layer capacitances through the bulk resistance of the sample; and, third, that this phenomenon leads to behavior that is similar to a Debye model for dipole orientation, but with an apparent permittivity (dielectric constant) that is inversely proportional to the boundary layer thickness, and, thus, can be much larger than the actual bulk permittivity of the material under measurement. Data are presented which demonstrate this effect with a DGEBA resin in the presence of blocking layers that vary in thickness from .0023 to 1.5 μm . The implications for the interpretation of data obtained while monitoring adhesive cure are discussed.

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INTERPRETATION OF DIELECTRIC CURE DATA IN ADHESIVES**

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ABSTRACT

The use of dielectric measurement techniques for monitoring the cure of adhesives and matrix resins used in composite materials is well known. Either parallel-plate electrodes or recently introduced dielectric microsensors can be used. During a typical cure, the quantitative results obtained from dielectric measurements early in cure, where the resin is a viscous liquid, have been shown to depend on the presence or absence of blocking layers at one or both electrodes. This paper reports a quantitative evaluation of the effects of blocking layers on the interpretation of such dielectric data. The approach follows that used for dilute electrolytes, which is a reasonable model for the liquid resins, in which ion conduction will always be present to some degree. It is shown, first, that blocking layers can be modeled as capacitances in series with the bulk adhesive; second, that when the dielectric loss factor of the material is high (which is typically true early in cure), the apparent dielectric response is dominated by the charging and discharging of boundary layer capacitances through the bulk resistance of the sample; and, third, that this phenomenon leads to behavior that is similar to a Debye model for dipole orientation, but with an apparent permittivity (dielectric constant) that is inversely proportional to the boundary layer thickness, and, thus, can be much larger than the actual bulk permittivity of the material under measurement. Data are presented which demonstrate this effect with a DGEBA resin in the presence of blocking layers that vary in thickness from .0023 to 1.5 μm . The implications for the interpretation of data obtained while monitoring adhesive cure are discussed.

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I. INTRODUCTION

Dielectric and conductivity measurements have been used to study chemical reactions in resins for more than 50 years [1]. Typically, an AC capacitance bridge or impedance meter is used in conjunction with a pair of electrodes, such as parallel plates or foils, or comb electrodes. Applications of such measurements to the cure of epoxy resins and other thermosets began in earnest in about 1958 [2,3]. A vast literature has developed since then, including studies of epoxies, phenolics, polyesters, and polyimides, to name a few, both as neat resins, and in structures such as fiber-resin composite laminates and adhesive joints. In 1981 a new integrated-circuit measurement technique was introduced, called Microdielectrometry, which combines comb electrodes with built-in amplification and temperature sensing in a single probe [4,5]. In all these measurements, the goal is to follow changes during cure in the dielectric permittivity ϵ' (dielectric constant), which for most resins ranges from 2 to 15, and in the dielectric loss factor ϵ'' , which can vary by many orders of magnitude, depending on the conductivity of the sample.

Parallel-plate and comb-electrode methods typically operate in the 10 Hz - 100 kHz range. The calibration of parallel-plate electrodes depends on plate spacing and area, as illustrated in an ideal case in Figure 1. Two plates of area A spaced apart by distance L and filled with a homogeneous medium having permittivity ϵ' and loss factor ϵ'' can be represented by an equivalent circuit having capacitance C and parallel resistance R given by:

$$C = \frac{\epsilon' \epsilon_0 A}{L} \quad R = \frac{L}{\omega A \epsilon'' \epsilon_0} \quad (1)$$

where ϵ_0 is the absolute permittivity of free space (8.85×10^{-12} F/m). Measurement of C and R at some angular frequency ω is then used to extract values for ϵ' and ϵ'' . Typical plate spacings for parallel-plate geometries are in the range of a few tenths of a mm to a few mm. If the spacing can change during cure, as might occur when pressure is applied to a laminate or adhesive joint, then the separate quantitative determination of both ϵ' and ϵ'' is not possible. As a result, it has been common practice to measure the ratio of ϵ'' to ϵ' , called the loss tangent ($\tan\delta$, which is also equivalent to the dissipation factor D of the parallel plate capacitor), because in the absence of blocking-electrode effects, the calibration of parallel plates for $\tan\delta$ is independent of plate spacing. In terms of the experimentally measured quantities, R and C, $\tan\delta$ is expressed as

$$\tan\delta = \frac{\epsilon''}{\epsilon'} = \frac{1}{\omega RC} \quad (2)$$

Since the geometrical quantities L and A cancel out of $\tan\delta$ when the medium is homogeneous, it has been widely assumed that all parallel-plate measurements of $\tan\delta$ are geometry-independent. However, one result of the present paper is to show that the conventional practice of placing a thin release film, which functions as a blocking layer, between parallel plates during cure studies can make the calibration depend directly on plate spacing, even when measuring only $\tan\delta$.

The comb electrodes, in contrast to parallel plates, do provide a fixed calibration both for ϵ' and ϵ'' , because electrode size and spacing does not change during cure. However, comb electrodes typically have limitations of sensitivity and frequency range due to practical instrumentation issues, and comb electrodes are also affected by blocking layer effects.

The Microdielectrometry approach, with interelectrode spacings measured in tens of μm , provides both the stable calibration of the comb electrode, and the ability to measure to arbitrarily low frequencies because of the built-in amplification. Microdielectrometry equipment is now available which covers the frequency range 0.005 Hz - 10 kHz.

The combination of low measurement frequency plus small interelectrode spacing of Microdielectrometry has brought out an effect, which while noticed in even the earliest conventional measurements [1], has only occasionally been analyzed in cure experiments [6]. The effect is the exact homologue of the polarization of blocking electrodes in electrolytes [7], and arises in the case of adhesives and resins from the ionic conductivity due either to intrinsic ions or to residual impurity ions. These ions are relatively mobile during the early portions of a typical cure sequence, when the sample viscosity is relatively low, and it is in this portion of the cure cycle that polarization effects are observed.

Figure 2 illustrates the effect. The permittivity measured using Microdielectrometry at a range of frequencies from 0.1 Hz to 10 kHz is shown as a function of cure time for an isothermal cure of DGEBA with DDS at 120 °C. Starting at about 200 minutes, the data show a clear sequence of classical dielectric relaxations at each frequency which is due to the increasingly hindered dipole orientation as vitrification is approached [8]. However, early in cure, and particularly at low frequencies, the measured permittivity is very large. The purpose of this paper is to demonstrate that this large apparent permittivity early in cure can be attributed to the polarization of blocking electrodes, and can be quantitatively modeled by assuming a blocking layer capacitance in series with the dielectric sample.

II. EXPERIMENTAL METHODS

The experiments consist of making dielectric measurements as a function of frequency on a non-curing sample material whose dielectric properties are varied by making temperature changes, and using a variety of electrode configurations and blocking layers. The sample material selected was Epirez 510^R, a commercial DGEBA resin with a dielectric permittivity at room temperature of 9, and with a residual ionic conductivity which could be varied

over many orders of magnitude by changing the temperature between 20 and 120 °C.

Two different electrode metals were used. Aluminum was used both for parallel-plate electrodes and as the electrodes on the Microdielectrometry probe. Gold was also used for parallel-plate measurements. For aluminum parallel-plate measurements, the interelectrode spacing was varied between 32 μm and 5 mm. For gold, a single 60 μm spacing was used. It should be noted that the smallest of these spacings (achieved by using Kapton^R film spacers) is much less than that typically used with parallel plates. No intentional blocking layers were used with the parallel plates; however, both metals yielded polarization characteristics indicating blocking behavior. Measurements on parallel-plate electrodes were made over the frequency range 10 Hz - 10,000 Hz with a GenRad 1689 Digibridge^R. In the case of the Microdielectrometry probe, the interelectrode spacing is fixed at 12 μm . However, blocking layer thickness was varied by spin-coating and curing films of DuPont 2555 polyimide onto some of the sensors prior to the measurements. Two polyimide thicknesses were used, 150 nm, and 1.2 μm . Microdielectrometry measurements were made over the same 10 - 10,000 Hz frequency range using equipment equivalent to the Micromet Instruments System II Microdielectrometer.

The typical experimental sequence involved placing a sample of the resin either between the parallel plates or on the Microdielectrometry probe, and measuring ϵ' and ϵ'' as a function of frequency at a series of temperatures between 20 and 120 °C. The primary effect of varying temperature is to vary the ionic conductivity of the resin. Thus, we were able to make a controlled change in the conductivity part of the dielectric properties of the sample without the complications of dipolar changes that would accompany a typical cure. This permits a clear isolation of the effects of polarization of blocking electrodes.

III. POLARIZATION MODEL

As a prelude to the presentation of experimental data, it is useful to examine a simple model of the polarization of blocking electrodes. Figure 3 illustrates the polarization schematically using the parallel-plate geometry. The sample is initially uncharged and unpolarized. When a voltage is applied to the plates, polarization proceeds both by dipole orientation (the normal permittivity) and by ionic conduction. If the electrodes are blocking, the ions accumulate at the electrodes, forming a charge layer which is qualitatively similar to the charge layer established by dipole orientation, but which can have a much greater charge per unit area. Thus, viewed from the electrodes, the measured capacitance C , which depends on the total polarization charge, can be much larger than would result from dipoles. Since the parallel equivalent circuit of Figure 1 is conventionally used to interpret dielectric measurements, the use of Equation 1 to extract ϵ' from C would result in an apparent permittivity which can be quite large.

A simple equivalent circuit that includes blocking layers is shown in Fig. 4. The two charge layers that form at the electrodes, each of thick-

ness t_b , are combined into a single blocking capacitor C_b with a plate spacing of $2t_b$. In order to distinguish between an apparent measured permittivity and the actual bulk permittivity of the medium, we shall denote the experimentally measured permittivity, loss factor, and loss tangent as ϵ'_x , ϵ''_x , and $\tan\delta_x$, respectively, where the x subscript represents an experimental result. These experimental values are what would be inferred from the measurement using the parallel R-C equivalent circuit of Fig. 1 together with Eq. 1. Quantities without the x subscript represent the actual values for the bulk resin, and are what would be measured when blocking layers are absent.

If we assume for simplicity that the permittivity within the blocking layer has the same value as that in the bulk, then C_b is given by

$$C_b = \frac{\epsilon' \epsilon_0 A}{2t_b} \quad (3)$$

The bulk permittivity is represented by a capacitor C as in Figure 1, and the ionic conductivity mechanism by a resistor R in parallel with C. If we allow for the blocking layer thickness, then the remaining thickness for the bulk portion of the sample is $L - 2t_b$. Hence, the value of C is

$$C = \frac{\epsilon' \epsilon_0 A}{L - 2t_b} \quad (4)$$

Assuming that the ionic conductivity σ is the only contribution to ϵ'' (i.e. $\epsilon'' = \sigma/\omega\epsilon_0$), then R is given by

$$R = \frac{L - 2t_b}{A\sigma} \quad (5)$$

The intrinsic loss tangent, $\tan\delta$, then becomes

$$\tan\delta = \frac{\sigma}{\omega\epsilon_0\epsilon'} \quad (6)$$

The critical issue is that when ionic conductivity is present, $\tan\delta$ can become arbitrarily large as the frequency is lowered. Therefore, when measuring at low frequencies early in cure (where relatively large ionic conductivity is present) the intrinsic $\tan\delta$ is large, and it is in this domain that polarization effects are observed. We now examine how this comes about.

Qualitatively, it is apparent that if the conductivity is low, hence making R large, the sample will behave as a simple dielectric with permittivity ϵ' . However, when the conductivity is large enough so that the impedance of R becomes less than that of C (the impedance of C is $1/\omega C$), then $\tan\delta > 1$ and the charging of C_b through R becomes the dominant behavior of the circuit. Under these circumstances, the relative impedances of R and C_b determine whether or not significant charging of C_b can take place at the frequency of measurement. As long as R represents the larger of the two impedances, then charging of C_b (i. e., electrode polarization) is not significant. However, when $R < 1/\omega C_b$, the charging of C_b becomes important. These arguments lead to two inequalities that must be satisfied if blocking layer effects are to be observed:

$$\tan\delta > 1 \quad (7)$$

and, by combining $R < 1/\omega C_b$ with Eqns. 3, 5, and 6

$$\tan\delta > \frac{L - 2t_b}{2t_b} \quad (8)$$

A useful method for demonstrating the effect of the blocking layer is with a plot of the experimental ϵ''_x vs ϵ'_x , with frequency as the parameter (a Cole-Cole plot). We have analyzed the circuit of Figure 4, and extracted the experimental ϵ'_x and ϵ''_x values using Equation 1. The results are

$$\epsilon'_x = \epsilon' \frac{L}{2t_b} \left[\frac{(\tan\delta)^2 + \left(\frac{L}{2t_b}\right)}{(\tan\delta)^2 + \left(\frac{L}{2t_b}\right)^2} \right] \quad (9)$$

$$\epsilon''_x = \epsilon'' \frac{L}{2t_b} \left[\frac{\left(\frac{L - 2t_b}{2t_b}\right)}{(\tan\delta)^2 + \left(\frac{L}{2t_b}\right)^2} \right] \quad (10)$$

$$\tan\delta_x = \frac{\epsilon''_x}{\epsilon'_x} = \tan\delta \left[\frac{\frac{L}{2t_b} - 1}{(\tan\delta)^2 + \frac{L}{2t_b}} \right] \quad (11)$$

It is interesting to note that in the ideal case of no blocking layer, i.e., $L \gg t_b$, the equations become $\epsilon'_x = \epsilon'$, $\epsilon''_x = \epsilon''$, $\tan\delta_x = \tan\delta$, as expected.

In these equations, the frequency appears implicitly in $\tan\delta$, with high frequencies corresponding to small $\tan\delta$ and low frequencies to large $\tan\delta$. Figure 5 shows a set of Cole-Cole plots illustrating the effect of the blocking layer thickness on the resulting dielectric parameters. For an infinitesimally thin blocking layer compared to the interelectrode spacing ($L/2t_b \gg 1$), the Cole-Cole diagram approaches a vertical line which intersects the ϵ'_x axis at the bulk (dipolar) permittivity ϵ' . As the ratio $L/2t_b$ decreases, either due to a smaller interelectrode spacing or a thicker blocking layer, the Cole-Cole diagram becomes semicircular, with one ϵ'_x -axis intercept at the bulk permittivity, and the second intercept at the bulk permittivity multiplied by $L/2t_b$. In the experimental discussion to follow, data of this type will be exhibited, and will be used to extract information about the blocking layer thickness t_b .

IV. EXPERIMENTAL RESULTS

Figure 6 shows Cole-Cole diagrams measured for the Microdielectrometer sensor with various thickness of blocking layers. It is seen that the Cole-Cole diagrams all show the semicircular characteristic of a blocking layer, with a common ϵ'_x intercept at the bulk permittivity, and a second intercept that moves to arbitrarily large ϵ'_x values as the blocking layer becomes thinner. Even in the case of the uncoated Microdielectrometer sensing electrodes, where the blocking layer thickness is measured in Angstroms (see below), the presence of the semicircular trend in the data is evident.

Figures 7 and 8 show parallel-plate results for various interelectrode spacings on aluminum and gold electrodes, respectively. In order to keep the plots of reasonable scale, some additional data points at higher values of ϵ'_x and ϵ''_x have been omitted from the diagrams; however, the solid lines are based on semicircular fits to all the data. The intercept of the semicircle is used to infer a blocking layer thickness for each interelectrode thickness.

We note first that in the case of the aluminum electrodes with the smaller interelectrode spacings, the various Cole-Cole plots yield good agreement on the value of t_b , which is 62 Å. This shows that it is reasonable to attribute a well defined blocking layer thickness to the resin-electrode interface. The corresponding value of t_b on gold electrodes (Fig. 8) is 23 Å. Since aluminum forms a native oxide and gold does not, one can attribute the thicker blocking layer on aluminum to the native oxide. Furthermore, using MacDonald's analysis of blocking layer capacitances in electrolytes [7], one can use the 23 Å thickness on gold to infer an equivalent ion concentration. That is, the intrinsic blocking layer thickness is estimated as equal to the Debye length L_D for the electrolyte, which is given by

$$L_D = \left[\frac{2kT\epsilon'\epsilon_0}{q^2 N} \right]^{1/2} \quad (12)$$

where kT is thermal energy, q is the electronic charge, and N is the ion concentration. Using a bulk permittivity of 9, the 23 Å blocking layer corresponds to an overall ion concentration of $4 \times 10^{18} \text{ cm}^{-3}$, or roughly 100 ppm, a reasonable value for residual impurities in a commercial resin.

V. DISCUSSION OF RESULTS

These results show that blocking layer effects can be observed in parallel-plate experiments when the $L/2t_b$ value becomes small enough. For conventional spacings without an added blocking layer, however, such as the 5mm spacing in Fig. 7, the Cole-Cole plot looks almost ideal. The problem is that it is common practice to add a release film which functions as an extrinsic block layer when doing dielectric cure monitoring. To show how important this effect can be, consider placing a 25 μm (one mil) blocking layer between 5 mm parallel plates. The ratio $L/2t_b$ in this case would be 100, which might appear to be large. However, the data of Fig. 7 clearly show significant blocking layer effects even when $L/2t_b$ is as large as 10,000. Therefore, much of the conventionally reported dielectric cure data, carried out with parallel plates in which a blocking layer is used have significant blocking layer effects in the data.

We can illustrate this effect for a hypothetical cure experiment by comparing $\tan\delta$ to the experimental $\tan\delta_x$ obtained from Equation (11). For illustration purposes, we assume that $\tan\delta$ begins at a low value, increases to a maximum, then decreases. This would be typical behavior in a ramped resin cure. Figure 9 shows a hypothetical cure behavior for $\tan\delta$ versus time together with the corresponding behavior of what would be the experimentally observed $\tan\delta_x$ for various values of $L/2t_b$. Note that as the blocking layer thickness increases, one changes from observing a maximum in $\tan\delta_x$ to a minimum. Furthermore, when there is a minimum in the experimental $\tan\delta_x$, two subsidiary maxima occur. Most important, since these blocking layer artifacts depend on the ratio of the interelectrode spacing to the blocking layer thickness, attempts to repeat parallel-plate cure studies without carefully controlling both the interelectrode spacing and blocking layer thickness could be expected to yield non-reproducible cure results.

There are many examples in the literature of data which resemble the $\tan\delta_x$ curves shown in Figure 9. As a result of this work, we are now re-examining much of the published data with a goal of clarifying the interpretation of the various $\tan\delta$ maxima and minima which have been reported. An evaluation of that literature will be the subject of a future publication.

VI. SUMMARY AND DISCUSSION

It has been demonstrated that the presence of capacitances at the boundaries of blocking electrodes affects the interpretation of dielectric measurements in materials which have ionic conductivity as the dominant polarization mechanism. Analysis of experimental data using Cole-Cole plots has shown that the polarization effect is determined by the ratio of the interelectrode spacing to the blocking layer thickness. Results from a range of electrode spacings were used to extract an intrinsic blocking layer thickness for a DGEBA resin, and a Debye-length interpretation of that thickness corresponds to reasonable levels of ionic contamination. It has been further shown that even in conventional parallel-plate measurements, if an extrinsic blocking layer is used, one must take careful account of blocking layer effects when interpreting dielectric data. In particular, for commonly used blocking layer thicknesses, maxima in the intrinsic $\tan\delta$ appear in the data as $\tan\delta_x$ minima, with the appearance of secondary maxima. Furthermore, the widespread practice of assuming that $\tan\delta$ calibration of parallel-plate measurements is independent of plate spacing may lead to non-reproducible results in cure studies where plate spacing and blocking layer thickness are not carefully controlled.

ACKNOWLEDGEMENTS

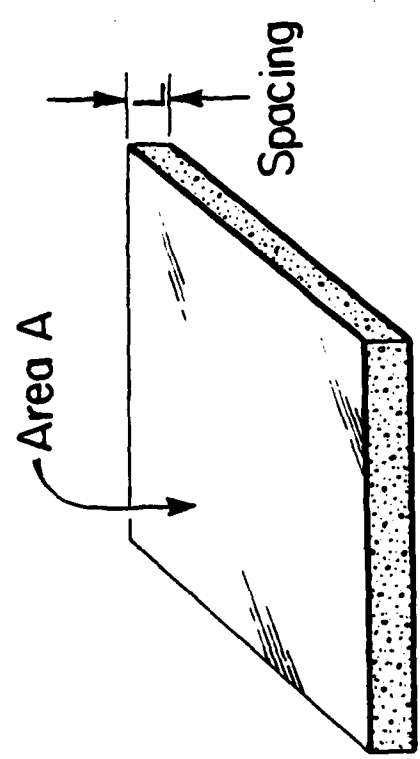
This work was supported in part by the Office of Naval Research. The authors are indebted to Norman F. Sheppard, Jr., for supplying the cure data of Figure 2, and for participation in many technical discussions. Discussions with Drs. Z Sanjana and A. Bennett (Westinghouse Research Laboratory) and Dr. L. H. Peebles, Jr., (ONR) during the early phase of this research are gratefully acknowledged.

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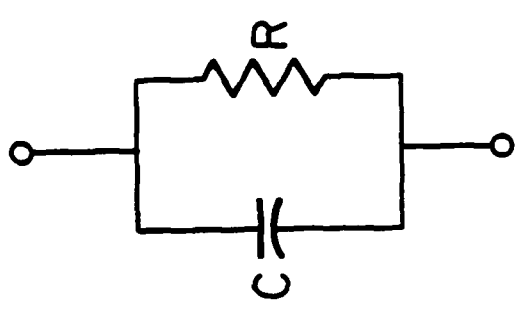
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FIGURE CAPTIONS

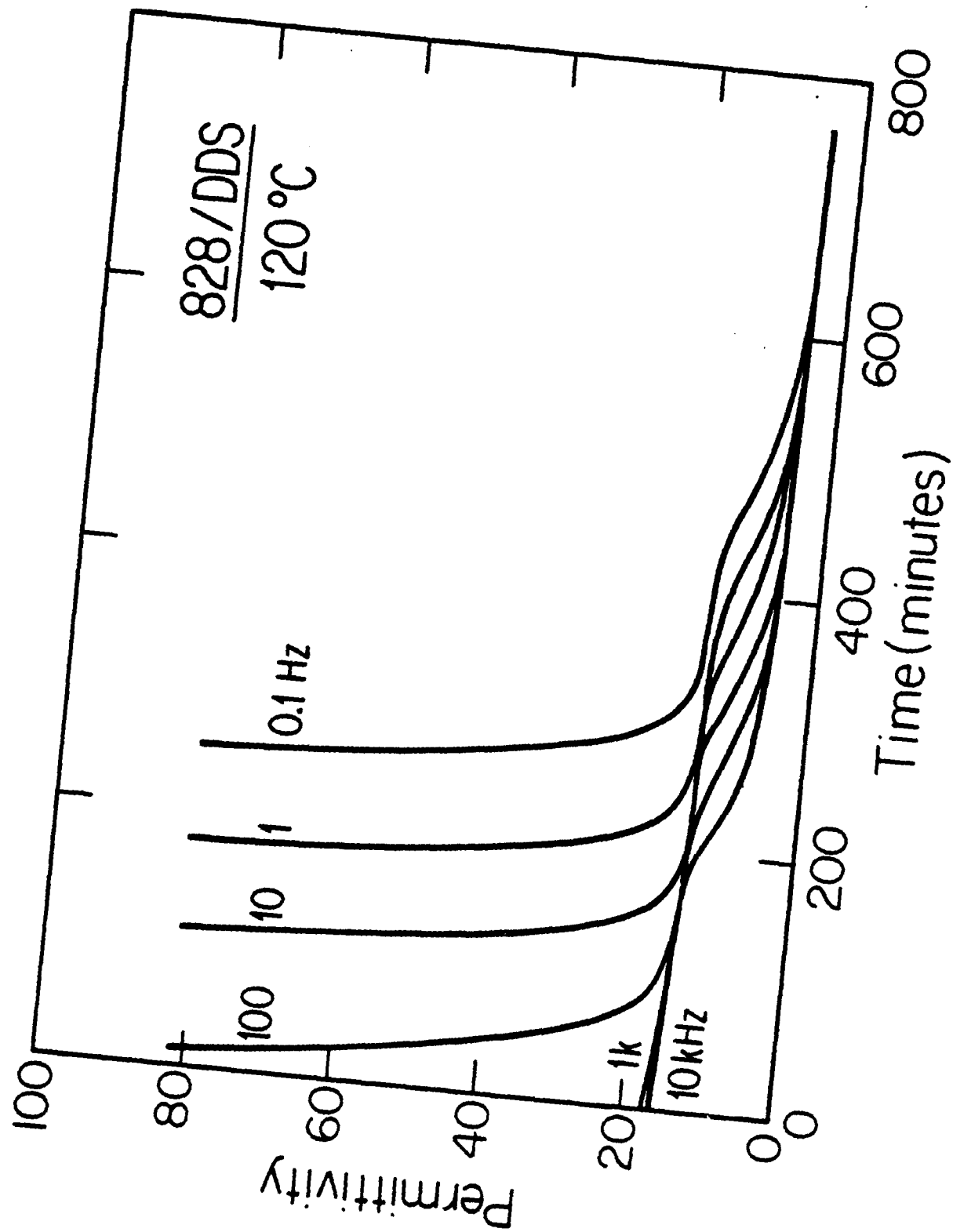
- Figure 1. (a) Schematic of ideal parallel-plate capacitor filled with homogeneous medium; (b) equivalent circuit.
- Figure 2. Typical experimental cure data in which blocking layer effects produce a large measured permittivity (ϵ'_x) early in cure, particularly at low frequencies.
- Figure 3. Schematic view of the polarization due to dipoles and ions: (a) unpolarized; (b) orientation and conduction begins; (c) fully polarized.
- Figure 4. Equivalent circuit that includes a blocking layer.
- Figure 5. Cole-Cole plots from Eqs. 9 and 10 for various $L/2t_b$.
- Figure 6. Experimental Cole-Cole plots from the Microdielectrometer.
- Figure 7. Experimental Cole-Cole plots from aluminum parallel plates with varied spacing.
- Figure 8. Experimental Cole-Cole plots from gold and aluminum parallel plates.
- Figure 9. Hypothetical cure data for $\tan\delta$ and for the corresponding $\tan\delta_x$ that would be observed experimentally for various values of $L/2t_b$.



(a)

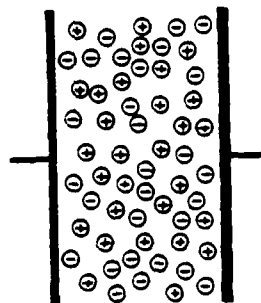
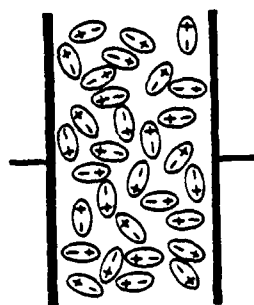


(b)



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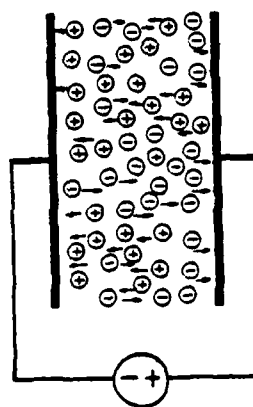
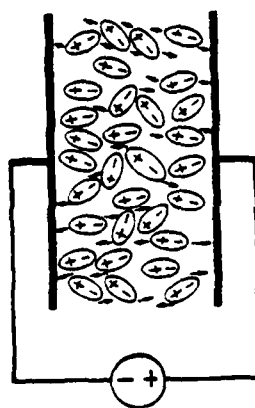
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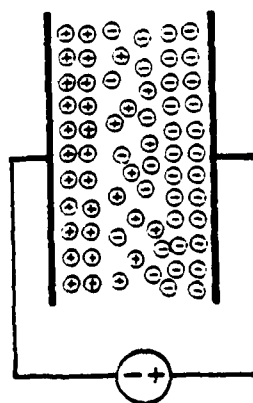
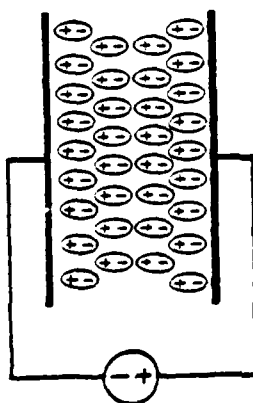
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(b)

POLARIZATION

POLARIZATION



(c)

